Claims

1. A polyurethane-polymer hybrid dispersion obtainable by

a) preparing a dispersion component or binder component based on an aqueous solution or dispersion of an optionally hydroxy- and/or amino-functional polyurethane-polymer hybrid having fluorinated or unfluorinated side chains, where

a_1) 5 to 100 parts by weight of an optionally laterally fluorine-modified, anionically stabilized polyurethane base dispersion (A) having preferably an ideally linearly segmented structure, a polymer-bonded fluorine content of 0 to 5% by weight, a hydroxyl number and/or amine number of 0 to 250 mg KOH/g, a solids content of 20% to 60% by weight, a solvent content of 0 to 20% by weight, and an average molar mass of 5000 to 100 000 daltons are admixed with 3 to 300 parts by weight of a monomer component (B) consisting of

(i) 1 to 100 parts by weight of one or more unsaturated monomers (B)(i) having one or more free-radically polymerizable double bonds, selected from the groups of acrylic acid and its derivatives and/or methacrylic acid and its derivatives and/or styrene and its derivatives

and/or

(ii) 1 to 100 parts by weight of one or more unsaturated fluorine-modified monomers

(B)(ii) having one or more free-radically polymerizable double bonds, selected from the groups of alkyl (per)fluoro (meth)acrylates and/or (per)fluoroalkyl (meth)acrylates and/or (per)fluoroalkyl (per)fluoro(meth)-acrylates and/or reaction products of 1-(1-isocyanato-1-methylethyl)-3-(2-propenyl)benzene (m-TMI) and perfluoroalkyl alcohols

and/or

(iii) 1 to 100 parts by weight of one or more unsaturated optionally fluorine-modified monomers (B)(iii) having one or more free-radically polymerizable double bonds, selected from the group of reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula $(RSiO_{1.5})_n$ with n = 4, 6, 8, 10, 12 and R = organic radical having 1 to 100 C atoms and 0 to 50 N and/or 0 to 50 O and/or 0 to 50 F and/or 0 to 50 Si and/or 0 to 50 S atoms and a molar mass of 250 to 25 000 daltons,

with 0.01 to 10 parts by weight of an initiator component (C), consisting of at least one lipophilic free-radical initiator having one or more thermally labile azo or peroxo groups, and 0 to 200 parts by weight of water, it being possible for the monomer component (B), the initiator component (C), and the water to be metered in simultaneously, successively or in a mixture to the polyurethane base dispersion (A), and subsequently

a_2) in the reaction mixture from stage a_1), as a result of the thermal decomposition of component (C), carrying out a free-radical polymerization of component (B) within the micelles of the polyurethane base dispersion (A),

and, if desired,

b) subsequently reacting the dispersion or binder component formed from components (A) to (C) from stage a_2) with 20 to 100 parts by weight of a crosslinker component (D) (curing agent), use being made as crosslinker component (D) of water-dispersible (paint) polyisocyanates having aliphatically and/or cycloaliphatically and/or aromatically attached isocyanate groups, it being possible for these polyisocyanates to contain 0 to 25% by weight of an organic solvent.

2. The polyurethane-polymer hybrid dispersion of claim 1, characterized in that as component (A) use is made of optionally hydroxy- and/or amino-functionalized polyurethane dispersions based on (hydrophobically modified) polyalkylene glycols, aliphatic or aromatic polyesters, polycaprolactones, polycarbonates, α,ω-polybutadienepolyols, α,ω-polymethacrylatediols, α,ω-dihydroxyalkylpolydimethylsiloxanes, macromonomers, telecheles, hydroxy-functional epoxy resins, oxidatively drying alkyd resins based on bisepoxides and unsaturated fatty acids, hydroxy-functional polysulfides or mixtures thereof.

3. The polyurethane-polymer hybrid dispersion of claim 1, characterized in that as component (A) use is made of polyurethane dispersions which contain as structural groups laterally fluorine-

modified macromonomers based on reaction products of

a) perfluoroalkyl alcohols, diisocyanates, and diethanolamine, use being made preferably of perfluoroalkyl alcohols having terminal methylene groups (hydrocarbon spacers) of the general formula

$$CF_3-(CF_2)_x-(CH_2)_y-OH,$$

with x = 3-20 and y = 1-6

or hexafluoropropene oxide (HFPO) oligomer alcohols of the general formula

$$CF_3CF_2CF_2O-(CF(CF_3)CF_2O)_z-CF(CF_3)CH_2-OH$$

with z = 1-10

or else mixtures of these,

and/or

b) perfluoroalkylalkenes and diethanolamine, use being made preferably of perfluoroalkylalkenes having terminal methylene groups (hydrocarbon spacers) of the general formula

$$CF_3-(CF_2)_x-CH_2=CH_2$$

with x = 3-20

or else mixtures of these,

and/or

c) alkyl (per)fluoro(meth)acrylates and/or (per)fluoroalkyl (meth)acrylates and/or (per)fluoroalkyl (per)fluoro(meth)acrylates and diethanolamine

and/or

d) (per)fluoroalkylalkylene oxides and N-methylethanolamine or diethanolamine.

4. The polyurethane-polymer hybrid dispersion of any one of claims 1 to 3, characterized in that as component (B)(iii) use is made of reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula $(RSiO_{1.5})_8$ with R = methacryloyloxypropyl and optionally $CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_3$ and/or H and/or C_1-C_{25} alkyl and/or C_3-C_{25} cycloalkyl and/or C_6-C_{30} aryl and/or $(CH_2)_3(OCH_2CH_2)_nOMe$ and/or aminopropyl and/or epoxypropyl and/or dimethoxysilyloxy and/or isocyanatopropyl and/or triethoxysilylpropyl.

5. The polyurethane-polymer hybrid dispersion of any one of claims 1 to 5, characterized in that as component (B)(iii) use is made of reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula

$$(R_aX_bSiO_{1.5})_m$$

where
a = 0 or 1,
b = 0 or 1,
a + b = 1,
m = 2, 6, 8, 10, 12, and
R = hydrogen atom, alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl or cycloalkynyl group or polymer unit, each of which are substituted or unsubstituted, or further functionalized polyhedral oligomeric silicon-oxygen cluster units, which are attached via a polymer unit or a bridging unit,
X = oxy, hydroxy, alkoxy, carboxy, silyl, alkylsilyl, alkoxysilyl, siloxy, alkylsiloxy,

alkoxysiloxy, silylalkyl, alkoxysilylalkyl, alkylsilylalkyl, halogen, epoxy, ester, fluoroalkyl, isocyanate, blocked isocyanate, acrylate, methacrylate, nitrile, amino, phosphine or polyether group or substituents of type R containing at least one such group of type X,

and the substituents of type R and also the substituents of type X being identical or different.

6. The polyurethane-polymer hybrid dispersion of any one of claims 1 to 5, characterized in that as component (C) use is made of a free-radical initiator which has a half-life of one hour at a decomposition temperature in the range from 40 to 120°C.

7. The polyurethane-polymer hybrid dispersion of any one of claims 1 to 6, characterized in that as component (C) use is made of 2,2'-azobis(2-methylbutyronitrile) and/or 2,2'-azobis(2-methylpropionitrile).

8. The polyurethane-polymer hybrid dispersion of any one of claims 1 to 7, characterized in that the initiator/monomer molar ratio of components (B) and (C) is set at a level of 0.001 to 0.05.

9. The polyurethane-polymer hybrid dispersion of any one of claims 1 to 8, characterized in that in the anionically modified polyurethane hybrid polymer formed from components (A) to (C) the amount of carboxylate and/or sulfonate groups is set at 5 to 25 meq·(100 g)$^{-1}$, preferably at 10 to 20 meq·(100 g)$^{-1}$, and the acid number at 2.5 to 15 meq KOH·g^{-1}, preferably at 5 to 12.5 meq KOH·g^{-1}.

10. The polyurethane-polymer hybrid dispersion of any

one of claims 1 to 9, characterized in that the solids content in terms of fluorine-modified polyurethane hybrid polymer consisting of components (A) to (C) is set at 30% to 70% by weight, preferably at 40% to 60% by weight, based on the total amount of the polyurethane-polymer hybrid dispersion.

11. The polyurethane-polymer hybrid dispersion of any one of claims 1 to 10, characterized in that the ratio of the proportional solids contents of (fluorine-modified) polyurethane resin from component (A) and (fluorine-modified) polymer resin from components (B) and (C) is set at 20%:80% to 80%:20% by weight, preferably at 40%:60% to 60%:40% by weight.

12. The polyurethane-polymer hybrid dispersion of any one of claims 1 to 11, characterized in that the polyurethane dispersions or polyurethane-polymer hybrid dispersions contain less than 10% by weight of organic solvents.

13. The polyurethane-polymer hybrid dispersion of any one of claims 1 to 12, characterized in that the average particle size of the micelles amounts to 50 to 500 nm, preferably 100 to 400 nm.

14. The polyurethane-polymer hybrid dispersion of any one of claims 1 to 13, characterized in that the average molar mass (number average) amounts to 50 000 to 500 000 daltons.

15. The polyurethane-polymer hybrid dispersion of any one of claims 1 to 14, characterized in that the ratio of crosslinker component (D) to the binder component comprising components (A) to (C) is 1:3 to 1:5.

16. A method of preparing the polyurethane-polymer hybrid dispersion of any one of claims 1 to 15, characterized in that a dispersion component is prepared by

a_1) optionally diluting an optionally fluorine-modified polyurethane base dispersion (A) with water and admixing it with a pre-prepared mixture of components (B) and (C) and also with water, it being possible to meter in the monomer component (B) or its individual constituents, the initiator component (C), and the water simultaneously, successively or in a mixture to the polyurethane base dispersion (A), and finally

a_2) carrying out a free-radical polymerization of component (B) by means of the thermal decomposition of component (C),

and also, if desired, by

b) reacting the binder component formed from components (A) to (C) from stage a_2) subsequently with 20 to 100 parts by weight of a crosslinker component (D).

17. The method of claim 16, characterized in that reaction stage a_1) is carried out at a temperature of 15 to 35°C, preferably at 20 to 30°C.

18. The method of either one of claims 16 and 17, characterized in that reaction stage a_2) is carried out at a temperature difference of ±10°C relative to the temperature at which component (C) has a half-life of 1 hour.

19. The method of any one of claims 16 to 18, characterized in that reaction stage a_2) is carried

out preferably at a temperature of 80 ± 10°C when using 2,2'-azobisisobutyronitrile as component (C).

20. The method of any one of claims 16 to 19, characterized in that the free-radical polymerization in reaction stage a_2) is carried out without further emulsifiers.

21. The method of any one of claims 16 to 20, characterized in that reaction stage b) is carried out at a temperature of 15 to 35°C, preferably at 20 to 30°C.

22. The utilization of the polyurethane-polymer hybrid dispersion of any one of claims 1 to 15, characterized in that it is used in one-component or two-component form.

23. The utilization of the polyurethane-polymer hybrid dispersion of claim 22, characterized in that, in the case of two-component application, formulated or unformulated polyurethane-polymer hybrid dispersion is used as binder component and water-emulsifiable (paint) polyisocyanates are used as curing component.

24. The utilization of the polyurethane-polymer hybrid dispersion of either one of claims 22 and 23 in the construction or industrial sector for the permanent oil- and water-repellent surface treatment or modification of mineral and nonmineral substrates, such as

a) inorganic surfaces,
such as porous, absorbent, rough, and polished building materials and construction materials of all kinds (such as concrete, gypsum, silica and silicates, artificial

stone, natural stone (such as granite, marble, sandstone, slate, and serpentine), clay, cement, brick) and also enamels, fillers and pigments, glass, ceramic, and metals and metal alloys,

b) organic surfaces,
such as wood and woodbase materials, wood veneer, glass fiber-reinforced plastics (GRP), plastics, leather, natural fibers, polar organic polymers of all kinds, and composite materials.

25. The utilization of the polyurethane-polymer hybrid dispersion of any one of claims 22 to 24 for permanent oil- and water-repellent surface treatment or modification of mineral and nonmineral substrates in the application fields of

construction, such as

- antigraffiti/antisoiling coatings,
- easy to clean coatings,
- other coatings of all kinds (such as balcony coatings, roof (shingle) coatings, baking varnishes, inks and paints, masonry paints, floor coatings, light-, medium- and high-duty industrial floors, car park surfacings, sports floors),
- seals,
- prefabricated concrete components,
- concrete moldings,
- tiles and joints,
- adhesives and sealants,
- soundproofing walls,
- corrosion control,
- renders and decorative plasters,
- exterior insulation and finishing systems (EIFS) and exterior insulation systems (EIS),

and also

non-construction and industrial, such as

- automobile industry,
- coil coatings,
- baking varnishes,
- glass frontages and glass surfaces,
- ceramics, including sanitary ceramics,
- leather dressing,
- surface-modified fillers and pigments,
- paper coating,
- rotors of wind turbines,
- marine paints.